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IRRADIATION EFFECT ON Er_2O_3/n-Si STRUCTURE UNDER HIGH GAMMA-RAY DOSE

Aysegul Kahraman[1*], Berk Morkoc[1], Alex Mutale[2], Umutcan Gurer[2], Ercan Yilmaz[2,3]

[1]Physics Department, Faculty of Arts and Sciences, Uludag University, Bursa, Turkey
[2]Physics Department, Faculty of Arts and Sciences, Abant Izzet Baysal University, Bolu, Turkey
[3]Center for Nuclear Radiation Detector Research and Applications, Abant Izzet Baysal University, Bolu, Turkey

Abstract. *The aim of this study is to investigate the structural transformations of erbium oxide (Er_2O_3) dielectric which can be used as a sensitive region in the new generation RadFET radiation sensors under a high gamma dose. The Er_2O_3 film was grown on n-type Si (100) by RF magnetron sputtering and film thickness was measured as 118 nm. The samples were irradiated by a ^{60}Co radioactive source with the doses of 1 kGy, 25 kGy, and 50 kGy. The crystal structure samples were analysed by the X-ray diffraction method. The variation in the bond properties of the as-deposited Er_2O_3 film was investigated by X-ray photoelectron spectroscopy. The pre-irradiation Er_2O_3 film demonstrated an amorphous structure, and the peaks belonging to the cubic phase were observed after irradiation, their density increasing with increasing the dose. The Er 4d spectra of the Er_2O_3/Si films were two fitted peaks indicating Er-Er and Er-O bonds, except for the interface. The binding energy shifted to higher energies with increasing the depth from due to possible $ErSiO_x$ formation at the interface. The Si-O/Er-O and M/O ratios change with the applied dose and film depth.*

Keywords: *Er_2O_3, MOS, irradiation effect, gamma dose, structural variation*

1. INTRODUCTION

The main disadvantage of the SiO_2-based RadFET (p channel MOSFET) radiation sensors, which are found in many areas, from radiotherapy clinics to radiation modules in the spacecraft, is that they cannot read the dose below 10 mGy with high accuracy [1]–[3]. The focus of most of the studies on FET-based microelectronic devices is to reduce device dimensions, using high-k dielectrics as the gate oxide layer [4], [5]. However, developments in this area have not yet been transferred to the radiation sensor field. Most of the studies to improve the sensitivity of RadFETs to low doses are carried out through MOS capacitors due to easy production. In this context, the dielectrics such as Hf-based oxides, rare earth oxides were studied and the sensitivities of the some high-k MOS capacitors were found to be higher to lower dose than SiO_2-based MOS device [6]–[9]. One of the most notable of these is the MOS devices based on Er_2O_3, which has a sensitivity of 61 mV/Gy in the dose range of 16-76 Gy [7]. As a result of the interaction of a typical MOS capacitor with radiation, the flat band and mid-gap voltages are expected to shift to the left compared to non-irradiated electrical characteristics due to the low mobility of positive charges with respect to negatives and the expected further trapping within the structure. Although the sensitivity of the MOS capacitor produced with Er_2O_3 film annealed at 500 ^oC is higher than many high-k based devices, a bidirectional shift in C-V curve was observed [7]. Another rare earth oxide Yb_2O_3 was studied in the amorphous structure and the C-V curve shifted continuously to the left with increasing the dose, as expected, indicating that positive charges were more trapped in the structure than the negative ones [6]. Identifying the causes of this unwanted behaviour in the Er_2O_3, the MOS capacitor is crucial to the development of next-generation RadFET radiation sensors.

The aim of this study is to determine the changes in the structural properties of Er_2O_3 under irradiation. For this purpose, Er_2O_3 films were enlarged on the n type Si with an RF magnetron scattering system and the annealing process was not applied to the structure similar to Yb_2O_3. The ^{60}Co radioactive source was used to irradiate the devices and structural analyses were performed with the X-ray diffraction method (XRD) and X-ray photoelectron spectroscopy (XPS). To the best of our knowledge, this is the first study examining the structural properties of as-deposited Er_2O_3 film under radiation.

2. EXPERIMENTAL PROCEDURE

The erbium oxide films were deposited on a 6-inch Si (100) wafer with the RF magnetron sputtering using the Er_2O_3 target with a purity of 99.99%. First of all, the possible contamination of the Si wafer was removed by following the standard RCA cleaning procedure and the wafers were dried with nitrogen gas.

* aysegulk@uludag.edu.tr

After cleaned, the wafers were placed into the vacuum chamber of the RF magnetron sputtering system, and the pressure was reduced to 6×10^{-4} Pa. Before the shutter on the wafer was turned on, the sputtering was performed at 300 W for approximately 1 h to remove the contamination of the target. During this process, argon was given to the system with a flow rate of 16 sccm and a pressure of 1 Pa. The shutter on the wafer was then opened and film deposition was performed for 18 min. The produced film thickness was measured as 118 nm by using the Angstrom Sun Spectroscopic reflectometer. After leaving a portion of the sample for pre-irradiation analysis, the remaining portion was irradiated under ^{60}Co radioactive source with a dose rate of 1.3 kGy/h at the doses of 1 kGy, 25 kGy and 50 kGy in the Turkish Atomic Energy Authority. The XRD analyses of the films were performed in the diffraction angle range of 10°-80°. The XPS analyses were conducted with Physical Electronics-PHI 5000 VersaProbe (Monochromatic Al K_α X-ray radioactive source-1486.6 eV). The bond structures and the percentage of atomic concentrations in the film were determined. The depth profile was obtained by using Ar^+ (1 keV) sputtering to investigate bonding structures in different layers of films. All spectra were corrected to C 1s-284.8 eV.

3. Results and discussion

The XRD spectra taken in the diffraction angle of 10°-80° of the Er_2O_3/Si structures irradiated at 1 kGy, 25 kGy, and 50 kGy were given in Figure 1. The 2θ values corresponding to the peaks were indexed according to the International Centre for Diffraction Data (ICDD) (card no: 76-0159). The unexposed Er_2O_3 film is an amorphous structure. The film was a cubic phase which started to be directed to a polycrystalline structure with 1 kGy of irradiation. The structure preferred the (222) orientation with increasing the dose as well as the peak intensity. No extra peaks or impurity were determined in the XRD spectra of the films. The grain size (crystallization degree) was calculated using the strongest peak from the Scherrer's expression [10].

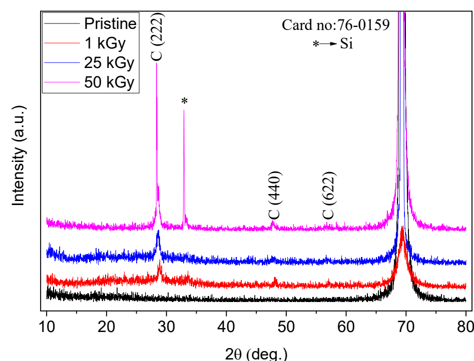

Figure 1. XRD spectra of the unexposed and exposed Er_2O_3 films

The grain sizes for 1 kGy, 25 kGy, 50 kGy were found to be 12.8 nm, 15.4nm, and 57.7 nm, respectively. These results demonstrate that the applied dose enhanced the crystal properties of the film because the energy is imparted to the media as the result of a number of collisions and the atoms rearrange due to local heating. On the other hand, the peaks related to reflections from the (440) and (622) planes of the cubic phase were also observed with an increasing dose.

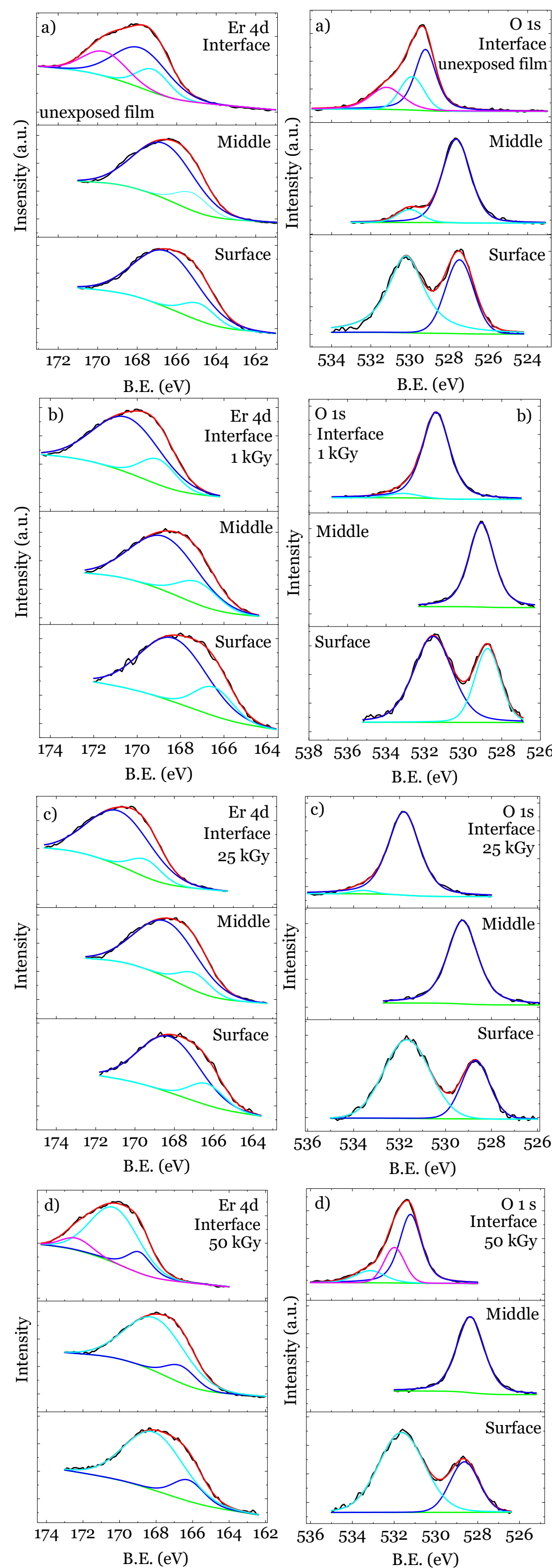

Figure 2. Er4d and O 1s XPS spectra of the Er2O3/Si a) unexposed; and irradiated at b) 1 kGy, c) 25 kGy, d) 50 kGy

The Er 4d and O1 s XPS spectra of the unexposed Er_2O_3/Si films are given in Figure 2.

The Er 4d spectra of the surface and mid of the unexposed film were deconvoluted into two Gaussian-Lorentzian (G-L) functions. The first peak at ~ 165.3 eV corresponds to metallic Er (Er-Er) [11], and the second peak at ~166.7 eV is assigned to Er^{3+} or oxygen bonding with erbium [12]. The binding energies of these peaks shifted to higher values at the interface, possibly caused by the diffused Si atom into the Er_2O_3 film [13]. Thus, a third peak, representing the formation of a silicate-like structure by deconvolution of the Er 4d spectrum of the interface, has emerged. The formation of Er-O-Si bonding (169.7 eV) causes a shift of the binding energy to higher value due to the high electronegativity of Si (χ_{Si}=1.9). O 1s spectra for the surface and mid of the film were deconvoluted into two G-L peaks, corresponding to Er-O bonding at 527.5 eV and hydroxyl species/-OH bonding (absorbed water vapour on film) at 530.1 eV [12], [14]. The O 1s spectrum obtained from the interface was fitted to three G-L peaks assigned to Er-O (529.2 eV), E-O-Si (529.9 eV) and Si-O (531.2 eV). The observation of the Si-O bonding, as well as the formation of $ErSiO_x$, indicates that the layer composed of only silicon dioxide was created during the deposition [12]. The atomic concentrations of the Er:O:C are 14.1:57.7:28.2 %. The reason for the oxygen-rich composition (O/Er=4.1) is high –OH bonding formation (Fig. 2b). The O/Er with incorporating carbon content of 0.13% is 1.87, resulting in an overstoichiometric film at the mid of the film. In this spectrum, –OH bonds, which were observed at low concentrations, caused an increase in oxygen content [12].

Metallic/oxygen bonding ratio (M/O) can give important information on oxygen vacancies/defects formation and these values were given in Table 1.

Table 1. The bond contents of the M/O and Si-O/Er-O at the interface

Sample		Si-O/Er-O	M/O
Pristine	Surface		0.188
	Mid of the film		0.204
	Interface	0.51	0.347
1 kGy	Surface		0.185
	Mid of the film		0.155
	Interface	0.05	0.246
25 kGy	Surface		0.184
	Mid of the film		0.159
	Interface	0.02	0.160
50 kGy	Surface		0.191
	Mid of the film		0.164
	Interface	0.40	0.240

No significant variations were observed among the M/O ratios obtained from the Er 4d spectra of the exposed and unexposed samples at the surface of the film because photons are likely to move through the material without interacting with the surface. The peaks assigned to metallic and oxygen bonding shifted to the higher binding energy of ~1.1 eV and ~1.6 eV, respectively. This shift can be associated with the enhancement of the crystal properties of the material. There is no significant difference between the binding energies of the peaks in the spectra obtained from the irradiated samples. Similar comments are valid for the O 1s spectra.

As far as the mid of the film is concerned, the peak representing the hydroxyl species disappeared because irradiation leads to heating in the oxide and evaporation of absorbed moisture, as in annealing. The Er 4d spectrum shifted to higher binding energies with 1 kGy of irradiation, and then slightly shifted to lower binding energies with increasing the dose. The O 1s spectrum assigned to Er-O bonding shifted to higher binding energies up to 25 kGy and changed direction at 50 kGy. The O/Er values for the 1 kGy, 25 kGy and 50 kGy are 1.50 (carbon content: 0%), 1.62 (carbon content: 3.5%) and 1.85 (carbon content: 0%), respectively. These results demonstrate that the stoichiometric erbium oxide is reached with the irradiation dose of 1 kGy, but the overstoichiometric film occurred with increasing the dose. The binding energy values for the erbium-oxygen bonding were given as 168.8 eV [12] and 168.4 eV [15]. The obtained binding energy of 168.6 eV after irradiation of 1 kGy is consistent with the literature values. The results may show that some defect centers were treated with irradiation of 1 kGy, but the Er_xO_y structure was formed with an increasing dose. The lowest M/O ratio was obtained from the sample irradiated at 1 kGy, and this ratio increased with increasing the radiation dose, indicating that the oxygen vacancies begin to form in the structure with increasing the dose. Therefore, binding energy shifted to lower values with increasing the dose with respect to 1 kGy.

For the interface, the Er 4d spectrum shifted to higher binding energies up to 50 kGy. The lowest M/O ratio was obtained from the sample irradiated at 25 kGy. Increasing this ratio at 50 kGy may indicate that oxygen vacancies/defect centers formed in the structure. On the side, Er 4d and o 1s spectra at 50 kGy were deconvoluted into three G-L peaks as the spectra of the unexposed film. The Si-O/Er-O ratio values were given in Table 1 and this ratio decreased at 25 kGy with respect to that of 1 kGy and increased at 50 kGy. It has been reported that positive charges at the oxide layer and interface are predominantly trapped compared to negatives in the process of SiO_2 interaction with radiation [16]. As can be seen from Table 1, the lowest value at 25 kGy may indicate negative charge traps at the interface. Both Er 4d and O 1s spectra shifted to higher binding energies compared to other layers due to approaching the Si layer.

4. Conclusion

The interaction mechanism of the Er_2O_3/Si structure with radiation was evaluated by the XRD and XPS techniques. The film, which displays an amorphous structure before irradiation, is in the cubic phase after irradiation. The grain size values increased with increasing the dose. The XPS spectra obtained from the surface of the film demonstrated that the gamma radiation did not cause a significant structural change on the surface due to their high penetrating power. The XPS spectra obtained from the mid of the film indicated that the density of the oxygen vacancies increased with increasing the dose. It can be concluded

from the silicate-like structure that the interface was eradicated with the irradiation of 1 kGy. Observation of the lowest Si-O/M-O and M/O ratios at 25 kGy at the interface or the absence of a general increase or decrease with irradiation may cause unexpected shifts in the electrical characteristics of the as-deposited Er_2O_3 based MOS device.

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